UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460
OFFICE OF CHEMICAL SAFETY AND
POLLUTION PREVENTION

MEMORANDUM

Date: June 11, 2013

Subject: **Dicamba.** Supplemental Residue Field Trial Studies For Dicamba in/on Sweet Corn to Support Petition PP# 0E6209 to Establish Permanent Tolerances.

Multi-Residue Method Testing to Address DCI for Dicamba RED to Support Reregistration.

PC Code: 029801, 029806	DP Barcode: D375578
Decision No.: 357484	Registration No.: 7969-242, 7969-150, 7969-132
Petition No.: 0E6209	Regulatory Action: N/A
Risk Assessment Type: N/A	Case No.: 0065
TXR No.: N/A	CAS No.: 1918-00-9
MRID No.: 48001303, 48001304, 48001305	40 CFR: 180.227

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Executive Summary

BASF Corporation has submitted three residue studies in response to the following:

- An Agency memorandum (D275611, 7/26/01, G. Kramer) of an Interregional Research Project No. 4 (IR-4) petition for uses of dicamba on sweet corn (PP# 0E6209) and,

- The Data Call In (DCI) for the Dicamba RED to support the reregistration of the herbicide dicamba (GPDCI-29801-27682).

The residue studies submitted by BASF included supplemental residue field trial studies at three locations, an LC/MS/MS analytical method used for data collection and multi-residue method recovery data for the dicamba metabolites of concern.

The field trial studies were conducted in the United States at the three locations specified in the memorandum (D 275611, G. Kramer, 7/26/2001). At each trial location, dicamba was applied as one foliar broadcast application of the WG formulation Status® at 0.125-0.127 lb ae/A (2× maximum application rate). Samples of corn forage, stover and sweet corn kernel plus cob with husks removed (K+CWHR) were harvested from all trials at mature (commercially acceptable RAC) and immature plant stages. Adequate data were available reflecting the stability of residues of dicamba and 5-OH dicamba under frozen storage conditions for the duration of the field trial studies.

Sweet corn samples were analyzed for residues of dicamba and its metabolite 5-OH dicamba using a validated Liquid Chromatography -Tandem Mass Spectrometry (LC-MS/MS); Method D0902. The limit of quantitation (LOQ; determined as the lowest limit of method validation, LLMV) was 0.01 ppm for all analytes in all sweet corn matrices. Overall recoveries of sweet corn matrices concurrently fortified at two concentration levels of 0.01 (LOQ) and 0.1 ppm, bracketing the expected residues, were 65-108% (average of 86% and standard deviation of 11%) for dicamba and 62-124% (average of 91% and standard deviation of 13%) for 5-OH dicamba.

In the three field trial studies, combined residues of dicamba and 5-OH dicamba were below the LOQ (<0.02 ppm) in/on all samples of K+CWHR and ranged between <0.02-0.09 ppm and <0.02-0.05 ppm in sweet corn forage and stover samples, respectively.

BASF Corporation also submitted multi-residue method data for the dicamba metabolites 5-OH dicamba and 3,6 dichloro salicylic acid (DCSA). The metabolites were screened through multi-residue methods described in the United States Food and Drug Administration (FDA) Pesticide Analytical Manual Volume I (PAM Vol. I). Testing through Protocol B revealed that partial recoveries were obtained for DCSA only on non-fatty food, but Protocol B was not suitable for 5-OH dicamba. Testing through Protocols A, C, D, E, and F showed that the protocols were not applicable to 5-OH dicamba because it was either not fully recoverable, or due to the lack of a fluorescence response. DCSA was not tested under Protocol D, E, or F because it did not show acceptable chromatographic separation under Protocol C. 5-OH dicamba and DCSA were not tested under Protocol G because the compounds are not substituted ureas.

Based on the data provided, the deficiencies in the residue chemistry requirements mentioned in the above memorandum and DCI are satisfied. The existing tolerance for residues of the herbicide dicamba and its 5-OH metabolite in/on sweet corn forage, K+CWHR and stover are appropriate.

1.0 Introduction

BASF has submitted three residue studies in response to an Agency memorandum (D275611, 7/26/01, G. Kramer) of an Interregional Research Project No. 4 (IR-4) petition for uses of dicamba on sweet corn (PP# 0E6209). HED had requested that the petitioner submit an additional three sweet corn residue trials conducted in Regions 1 (1 trial), 5 (1 trial) and 11 (1 trial), since the previously submitted nine sweet corn field trials did not match the number and locations required in OCSPP Harmonized Guidelines 860.1500: Crop Field Trials. In addition, translation of field corn forage and stover data could not be transferred to sweet corn because the application rate in the field corn trials was >10× the maximum sweet corn application rate.

The residue studies submitted by BASF included an LC/MS/MS analytical method (MRID 48001303), which was used for data collection in the sweet corn crop field trial study (MRID 48001305) as well as multi-residue testing data for the dicamba metabolites of concern [3,6-dichloro-5-hydroxy benzoic acid (5-OH dicamba) and 3,6-dichlorosalicylic acid (DCSA), MRID 48001304] in response to the Dicamba Reregistration Eligibility Document's (RED, D317699, D317703) request for multi-residue method recovery data for the dicamba metabolites of concern to support the reregistration of the herbicide dicamba.

2.0 Regulatory Recommendations

There are no residue chemistry considerations that preclude establishing permanent tolerances for residues of dicamba and its 5-OH metabolite in/on sweet corn raw agricultural commodities (RACs). Based on the additional data provided, the existing tolerance for residues of the herbicide dicamba and its 5-OH metabolite are appropriate:

Corn, sweet, forage	0.50 ppm
Corn, sweet, kernel plus cob with husks removed	0.04 ppm
Corn, sweet, stover	0.50 ppm

2.1 Data Deficiencies/Data Needs

There are no residue chemistry deficiencies

3.0 Crop Field Trials (860.1500)

Three new field trials were conducted in the United States during the 2008 growing season in the North American Free Trade Agreement (NAFTA) Zones 1 (NY; 1 trial), 5 (NE; 1 trial), and 11 (ID; 1 trial). The number and location of all field trials are listed in Appendix 2. Each trial consisted of one untreated plot and one treated plot. All treatment applications were made using a multiple active ingredient (MAI) water dispersible granule (WG) formulation of Status® Herbicide, EPA Reg. No. 7969-242, (containing 44% dicamba sodium salt (40% dicamba acid equivalents), and includes the co-active ingredient diflufenzopyr sodium salt, 17.1%, and isoxadifen-ethyl, which improves the safety of dicamba on corn. The samples were neither analyzed for diflufenzopyr, nor for isoxadifen-ethyl. At each trial location, dicamba was applied at one foliar broadcast application at 0.125-0.127 lb acid equivalent (ae)/A in spray volumes of

20-40 gal/A (2× maximum application rate) when the corn plant was 10-12 inches tall. A non-ionic surfactant (NIS) mixed with an ammonium sulfate liquid fertilizer was added to each spray mixture. The use pattern of Status® Fungicide in this study is found in Appendix 1.

The field trial study on sweet corn previously reviewed by the Agency (D 275611, 7/26/01, G. Kramer) included nine field residue trials and was conducted in 1996. Applications were made using the dicamba formulation; Distinct® (BAS 662 H, EPA Reg. No. 7969-150), which is also a multiple active ingredient water-dispersible granule (WG) formulation but containing 21.4% diflufenzopyr and 55% dicamba (50% dicamba acid equivalents). Field treatments consisted of two applications of Distinct® at a rate of 0.125 lb ae/A each, for a total application rate of 0.25 lb ae/A (1.3× maximum application rate). The first application was made when the corn plant was 12 inches tall, while the second application was made when the plant was 24 inches tall. Both applications were 2 weeks apart according to the label instructions. A summary of the residue data in these field trials are included with the residues in the three new field trials in Table 1.

In the new field trials, samples of corn forage and sweet corn kernel plus cob with husks removed (K+CWHR) were harvested from all trials at pre-harvest intervals (PHI) of 32-33 and 53-72 days and stover samples were harvested at PHIs of 72 and 88-98 days. The K+CWHR and stover samples taken at the first sampling interval were generally immature; however, those taken at the last sampling interval were commercially acceptable RAC samples.

Sweet corn samples were analyzed for residues of dicamba and its metabolite 5-OH dicamba using Liquid Chromatography -Tandem Mass Spectrometry (LC-MS/MS); Method D0902, which is described below. The limit of quantitation (LOQ; determined as the lowest limit of method validation, LLMV) was 0.01 ppm for all analytes in all sweet corn matrices. The method was verified prior to and in conjunction with sample analysis and is considered adequate based on acceptable method validation and concurrent recovery data. Two fortification levels were used in concurrent method recovery, which were adequate to bracket expected residue levels.

Samples were stored frozen (<-5 °C) from collection to analysis for 175-242 days (5.8-8.0 months) for forage, 156-199 days (5.1-6.5 months) for stover, and 178-244 days (5.9-8.0 months) for K+CWHR. Samples were analyzed within 0-3 days of extraction. Adequate storage stability data were available reflecting the stability of residues of dicamba and 5-OH dicamba under frozen storage conditions in/on field corn forage, silage, grain, and fodder for up to 3 and 2 years, respectively (D 317699, 12/20/05, C. Olinger). These data are adequate to support the storage conditions and durations of samples from the submitted field trials.

In the new field trials, combined residues of dicamba and 5-OH dicamba were below the LOQ (<0.02 ppm) in/on all samples of K+CWHR at 32-33 and 53-72-day PHI. In corn forage, the combined residues were <0.02-0.09 ppm and <0.02-0.07 ppm at 32-33 and 53-72- day PHI, respectively. In corn stover the combined residues were <0.02-0.05 at both 72 and 88-98- day PHI. In the previous field trials, the combined residues were <LOQ(<0.04)-0.34 ppm in forage at 28-56 day PHI, <0.04-0.37 ppm in stover at 35-112 day PHI and <0.04 ppm in ears (kernel plus cob with husk removed, K+CWHR) at 28-56 day PHI.

Between the 9 sweet corn field trials previously reviewed and the three additional trials submitted to address this data gap, HED concludes that the number of trials and their geographical distribution are adequate to support the established dicamba tolerances for sweet corn RACs. Both sets of trials involved dicamba application at a rate of 0.125 lb ae/A, with a 32-day PHI for sweet corn ears; however, 9 trials reflected use of two applications of dicamba, while 3 trials reflected use of just one application. While it would have been preferable for all trials to have used two applications, in view of the lack of persistence of dicamba residues, HED considers it unlikely that a 2nd application (corresponding to the equivalent of a 46-day PHI [32 day PHI + 14 day RTI]) would have significantly increased residue levels found in the three recent trials. Thus, because no combined residues of dicamba + 5-OH dicamba were detected in the 9 field trials using Distinct® or in the 3 field trials using Status® in sweet corn K+ CWHR (ears), and the highest combined residues obtained from all 12 trials in/on feedstuffs (forage and stover) at all collection times were well below established tolerances, the current tolerances for dicamba on sweet corn are adequate. HED now considers the dicamba sweet corn data deficiency to be resolved.

Conclusions

The number and locations of the submitted field trials were conducted according to the recommendation cited in the memorandum (D 275611, G. Kramer, 7/26/2001). The Agency considers that the requirements of OCSPP Harmonized Guidelines 860. 1500: Crop Field Trials are satisfied for the use of Status® and Distinct ®on sweet corn. Since the highest combined residues obtained from all 12 trials in/on all sweet corn matrices were below the established tolerances, the current tolerances for dicamba on sweet corn are adequate

TABLE 1. Summary of Residue Data from Sweet Corn Crop Field Trials with Dicamba[1].

Commodity	Formulation/Total App. Rate (lb ae/A)	PHI (days)	Residue Levels (ppm)[1]							
			n[2]	Sample Min.	Sample Max.	LAFT[2]	HAFT[2]	Median	Mean	Std. Dev.
Dicamba										
Forage	Status® Single application of 0.125-0.127	32-33	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A[3]
		53-72	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Immature K+CWHR		32-33	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
K+CWHR		53-72	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Immature stover		72	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Stover		88-98	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Forage	Distinct® 2 applications of 0.125	28-56	9	<0.02	0.1	0.02	0.06	0.02	0.03	0.0203
K+CWHR (ears)		28-56	9	<0.02	<0.02	0.02	0.02	0.02	0.02	N/A
Stover		35-112	9	<0.02	0.05	0.02	0.045	0.02	0.0256	0.0109
5-OH dicamba[4]										
Forage	Status® Single application of 0.125-0.127	32-33	3	<0.01	0.0786	0.01	0.0682	0.0100	0.0294	0.0336
		53-72	3	<0.01	0.0588	0.01	0.0579	0.0108	0.0262	0.0274
Immature K+CWHR		32-33	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
K+CWHR		53-72	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Immature stover		72	3	<0.01	0.0351	0.01	0.0293	0.0193	0.0195	0.0097
Stover		88-98	3	<0.01	0.0425	0.01	0.0316	0.0131	0.0182	0.0117
Forage	Distinct® 2 applications of 0.125	28-56	9	<0.02	0.2891	0.0186	0.2564	0.0653	0.0958	0.0785
K+CWHR (ears)		28-56	9	<0.02	<0.02	0.02	0.02	0.02	0.02	N/A
Stover		35-112	9	<0.02	0.3170	0.0186	0.2704	0.02	0.0775	0.1052
Combined Residues[5]										
Forage	Status® Single application of 0.125-0.127	32-33	3	<0.02	0.0886	0.02	0.0782	0.0200	0.0394	0.0336
		53-72	3	<0.02	0.0688	0.02	0.0679	0.0208	0.0362	0.0274
Immature K+CWHR		32-33	3	<0.02	<0.02	0.02	0.02	0.02	0.02	N/A
K+CWHR		53-72	3	<0.02	<0.02	0.02	0.02	0.02	0.02	N/A
Immature stover		72	3	<0.02	0.0451	0.02	0.0393	0.0293	0.0295	0.0097
Stover		88-98	3	<0.02	0.0525	0.02	0.0416	0.0231	0.0282	0.0117
Forage	Distinct® 2 applications of 0.125	28-56	9	<0.04	0.3391	0.0386	0.3064	0.0853	0.1258	0.0900
K+CWHR (ears)		28-56	9	<0.04	<0.04	0.04	0.04	0.04	0.04	N/A
Stover		35-112	9	<0.04	0.3670	0.0386	0.3154	0.0386	0.1031	0.1159

[1] Summary residue data from previous 9 field residues studies previously reviewed by the Agency and newly submitted 3 field trials for a total of 12 field residue trials.

[2] Except for sample min/max, values reflect per trial averages; n = no. of field trials. For calculation of median, mean, and standard deviation, the LOQ is 0.01 ppm for all analytes for the newly submitted 3 field trials and 0.02 for the previously reviewed 9 field trials. LOQ values were used for any results reported as <LOQ. LAFT = lowest-average-field-trial; HAFT = highest-average-field-trial.

[3] N/A = Not applicable.

[4] Residues of 5-OH dicamba are expressed in parent equivalents using a molecular weight conversion factor of 0.9325.

[5] Combined residues are the sum of dicamba and 5-OH dicamba.

4.0 Residue Analytical Methods (860.1340)

4.1 Data Collection Methods

BASF Corporation has submitted a high performance liquid chromatography method with tandem mass spectrometric detection (LC/MS/MS), BASF method D0902, for the determination of dicamba and the metabolite 5-hydroxy dicamba (5-OH dicamba) in/on corn forage, kernel plus cob with husk removed (K+CWHR), and stover. The method was used for data collection in the newly submitted sweet corn crop field trial study.

Briefly, homogenized samples are heated with 1 N HCl at ~90 °C for ~45 minutes. The extract is cooled to room temperature and filtered, then adjusted to volume with water. An aliquot of the extract is adjusted to pH 9-10 with concentrated NH_4OH, vortexed, and adjusted to pH 3-4 with concentrated formic acid. Sodium chloride is added, and the extract is partitioned twice with hexane:ethyl acetate (1:1, v:v) followed by centrifugation. The resulting organic phase is reduced to dryness under nitrogen, then reconstituted in methanol:water (10:90, v:v) for analysis by LC/MS/MS. The precursor/product ion transitions monitored for dicamba originated from the same ion fragment at *m/z* 218.9 and were 218.9 →174.8 and 220.9→176.8 (the isotope of *m/z* 218.99 → the isotope of *m/z* 174.8). However, two different precursor/product ion transitions were monitored for 5-OH dicamba at *m/z* 234.9→154.9 and 234.9→190.7. The first set of transitions is monitored for quantitation purposes, and the second set of transitions is monitored for confirmatory purposes. The method includes different mobile phase gradients developed to address significant matrix interferences. The limit of quantitation (LOQ; determined as the lowest level of method validation, LLMV) is 0.01 ppm for both analytes in all corn matrices.

The method was adequately validated in samples of sweet corn forage, K+CWHR, and stover fortified with a mixed standard of dicamba and 5-OH dicamba at two concentration levels of 0.01(LOQ) and 0.10 ppm. Overall recoveries were 65-108% (average of 86% and standard deviation of 11%) for dicamba and 62-124% (average of 91% and standard deviation of 13%) for 5-OH dicamba. The fortification levels used in method validation are adequate to bracket expected residues in sweet corn matrices. Table 2 lists the recovery results from the method validation.

Conclusion

The LC/MS/MS method used for data collection in the new sweet corn crop field trials adequately determines residues of dicamba and 5-OH dicamba in corn forage, K+CWHR, and stover. Acceptable method validation data were submitted and the fortification levels used in method validation bracketed the expected residues in sweet corn matrices.

TABLE 2. Recovery Results from Method Validation of dicamba in/on Corn Forage, K+CWHR, and Stover using the Data Gathering Analytical Method.

Matrix	Mobile Phase Gradient[1]	Spiking Level (ppm)	Quantitation[2]		Confirmation[3]	
			Recoveries Obtained (%)	Mean Recovery ± Std. Dev. [CV] (%)	Recoveries Obtained (%)	Mean Recovery ± Std. Dev. [CV] (%) CV
Dicamba						
Forage	I	0.01	NR/NC[4]	NR/NC	82, 88, 83, 74, 77	81 ± 6 [7]
	III		100, 97, 99, 97, 103	99 ± 3 [3]	85, 91, 90, 101, 95	92 ± 6 [7]
	I	0.10	NR/NC	NR/NC	95, 82, 81, 77, 75	82 ± 8 [9]
	III		105, 108, 103, 99, 102	103 ± 3 [3]	98, 101, 105, 94, 103	100 ± 5 [5]
K+CWHR	I	0.01	80, 86, 89, 78, 79	82 ± 5 [6]	90, 94, 89, 96, 75	89 ± 8 [9]
		0.10	80, 85, 85, 77, 86	83 ± 4 [5]	90, 92, 74, 88, 90	87 ± 7 [8]
Stover	IIB	0.01	65, 69, 79, 65, 69	69 ± 6 [8]	NR/NC	NR/NC
		0.10	72, 82, 86, 85, 74	80 ± 6 [8]	NR/NC	NR/NC
	III	0.01	NR/NC	NR/NC	79[5], 76[5], 84, 80, 80	80 ± 3 [4]
		0.10	NR/NC	NR/NC	85, 88, 93, 69, 75	82 ± 10 [12]
5-OH Dicamba						
Forage	I	0.01	79, 73, 86, 74, 73	77 ± 6 [8]	82, 86, 88, 84, 86	85 ± 2 [3]
	III		91, 89, 80, 96, 74	86 ± 9 [10]	102, 110, 85, 89, 92	96 ± 10 [11]
	I	0.10	99, 91, 100, 99, 92	96 ± 4 [5]	89, 102, 94, 100, 100	97 ± 6 [6]
	III		101, 99, 104, 105, 110	104 ± 4 [4]	91, 89, 115, 124, 89	102 ± 17 [16]
K+CWHR	I	0.01	76, 70, 87, 90, 73	79 ± 9 [11]	105, 115, 82, 114, 98	103 ± 13 [13]
		0.10	106, 86, 103, 94, 107	99 ± 9 [9]	92, 99, 101, 86, 84	93 ± 8 [8]
Stover	IIB	0.01	76, 71, 65, 82, 81	75 ± 7 [9]	NR/NC	NR/NC
			NR/NC	NR/NC	80[5], 62[5], 75, 70, 70	71 ± 6 [9]
	IV	0.10	81, 87, 101, 102, 93	93 ± 9 [10]	NR/NC	NR/NC
			NR/NC	NR/NC	108, 106, 91, 76, 102	96 ± 13 [14]

[1] Gradients I, II, IIB, and III are water and methanol, each containing 0.1% formic acid; Gradient IV is water containing 0.1% acetic acid and 2.5 mM dibutyl ammonium acetate and methanol containing 1% acetic acid.
[2] Monitored ion transitions were *m/z* 218.9→174.8 for dicamba and 234.9→154.9 for 5-OH dicamba.
[3] Monitored ion transitions were *m/z* 220.9→176.8 for dicamba and 234.9→190.7 for 5-OH dicamba.
[4] NR/NC = Not reported or not conducted.
[5] Mean of replicate analyses.

4.2 Enforcement Method

Adequate enforcement methods are available for determining residues of dicamba and 5-OH dicamba in crop commodities (Residue Chemistry Chapter of the Dicamba RED, D 317699, 12/20/05, C. Olinger).

4.3 Multi-Residue Methods (MRM) (860.1360)

BASF Corporation has submitted multi-residue testing data for the dicamba metabolites of concern [3,6-dichloro-5-hydroxy benzoic acid (5-OH dicamba) and 3,6-dichlorosalicylic acid (DCSA)] (MRID 48001304) in response to the Data Call In (DCI) for the Dicamba RED to support the reregistration of the herbicide (GDCI-29801-27682). The metabolites were screened through multi-residue methods described in the United States Food and Drug Administration (FDA) Pesticide Analytical Manual Volume I (PAM Vol. I).

Because the test substances are not substituted ureas, testing under Protocol G was not conducted. Testing through Protocol A was conducted for both substances; however, testing was suspended due to the lack of a fluorescence response at the excitation and emission wavelengths of 288 and 330 nm. Under Protocol B testing, DCSA was successful through the complete method with partial recovery in soybean forage fortified at 0.05 and 0.5 ppm. Protocol B described in PAM Vol. I may be applicable for determination of DCSA on non-fatty food. Protocol C testing of 5-OH dicamba indicated that further testing using Protocols D, E, and F was required. Because the ECD detector was determined to be most appropriate for the test compounds, the recovery of the compounds through the Florisil column cleanup procedures was evaluated first under Protocol D. 5-OH dicamba was not recoverable from the Florisil column cleanup procedures under Protocols D, E, and F.

Conclusion

The metabolites of dicamba, 5-OH dicamba and DCSA were adequately evaluated for recovery through FDA multi-residue methods and showed that both metabolites are unsuitable for all Protocols tested, except DCSA, which may be recovered in non-fatty foods using Protocol B.

TABLE 3. Results of Multi-residue Methods Testing with Dicamba Metabolites (5-OH dicamba and DCSA).

PAM I Protocol	Analyte	Results	Comments
A	5-OH-dicamba 3,6-dichlorosalicylic acid (DCSA)	Subjected to testing under Module DL2 and neither compound fluoresced at excitation and emission wavelengths of 288 and 330 nm.	Protocol A is not applicable for analysis of 5-OH dicamba and DCSA.
B	5-OH-dicamba	Methylated according to Protocol B and was found to produce a signal under Module DG1. Acceptable recovery was found for both the GPC and Florisil cleanups, however, recoveries through the complete method on both non-fatty food (soybean forage) and fatty food (soybean seeds) were low (≤6%) or zero.	Protocol B is not applicable for analysis of 5-OH dicamba.
	DCSA	Methylated according to Protocol B and was found to produce a signal under Module DG1. Acceptable recovery was found for both the GPC and Florisil cleanups. Recoveries through the complete method on non-fatty food (soybean forage) were 38.5-61.1%, however, recoveries for fatty food (soybean seeds) were low at 0-3.4%.	Partial recoveries were obtained for DCSA in soybean forage fortified at 0.05 and 0.5 ppm. Based on these results Protocol B may be applicable for analysis of DCSA on non-fatty food.
C	5-OH dicamba	Subjected to testing under Section 302, using modules DG-1 (electron capture detection; ECD with Equity-1 column) and DG-13 (ECD with DB-17 column). In module DG-1, the instrument produced multiple inconsistent peaks indicating thermal degradation. In module DG-13, 50% full-scale deflection (FSD) was achieved at a concentration of 1.24 ng with a relative retention time (rrt; chlorpyrifos) of 0.66 minutes.	Based on the results of Protocol C testing, further testing through Protocols D, E, and F was required. The results indicated that the best detector for 5-OH dicamba is the ECD.
	DCSA	Subjected to testing under Section 302, using modules DG-1 (ECD with Equity-1 column) and DG-13 (ECD with DB-17 column). In module DG-1 and DG-13, the instrument produced multiple inconsistent peaks indicating thermal degradation.	Protocol C is not applicable for analysis of DCSA.
D	5-OH dicamba	Because 5-OH-Dicamba was chromatographable in Protocol C testing with ECD, recovery through Florisil was investigated. Recoveries through both cleanup tests, Section 302 C1 and Section 302 C5, were 0%. No further testing was conducted.	Protocol D is not applicable for analysis of 5-OH dicamba.
	DCSA	Not tested.	
E	5-OH dicamba	Because 5-OH-Dicamba was chromatographable in Protocol C testing with ECD, recovery through Florisil was investigated. Recoveries through both cleanup tests, Section 303 C1 and Section 303 C2, were 0%. No further testing was conducted.	Protocol E is not applicable for analysis of 5-OH dicamba.
	DCSA	Not tested.	
F	5-OH dicamba	The Florisil cleanup test in Protocols E (Sec. 303 C1 and C2) and F (Sec. 304 C1 and C2) are identical. Only one test was done for both. No further testing was conducted.	Protocol F is not applicable for analysis of 5-OH dicamba.
	DCSA	Not tested.	
G	5-OH dicamba DCSA	Not tested.	Test substances are not a substituted urea.

Appendix 2. Updated Trial Numbers and Geographical Locations.			
NAFTA Growing Regions	Sweet Corn		
	Submitted (total)	Requested[1]	
		Canada	U.S.
1	2[2]	--	2/1
1A	--	--	--
2	1	--	1/1
3	1	--	1/1
4	--	--	--
5	4[2]	--	5/3
5A	--	--	--
5B	--	--	--
6	--	--	--
7	--	--	--
7A	--	--	--
8	--	--	--
9	--	--	--
10	1	--	1/1
11	1[2]	--	1/1
12	2	--	1/1
13	--	--	--
14	--	--	--
15	--	--	--
16	--	--	--
17	--	--	--
18	--	--	--
19	--	--	--
20	--	--	--
21	--	--	--
Total	12	--	12/9

[1] As per Table 5 of 860.1500 for sweet corn; the second number reflects a 25% reduction in the number of field trials allowed for the crop as a representative commodity in support of a crop group/subgroup tolerance or when application results in no quantifiable residues.

[2] New studies submitted using Status®, one trial in each indicated growing region

Appendix 1. Status® Fungicide Use Pattern.

Location County, State; Year (Trial ID)	EP[1]	Application					Tank Mix/ Adjuvants[3]
		Method; Timing	Volume gal/A	Rate (lb ae/A)	RTI[2] (days)	Total Rate (lb ae/A)	
Wayne, NY; 2008 (RCN R080608)	40% WG	Foliar broadcast; BBCH 15, 5 leaves (~10-12" tall)	40	0.1268	--	0.1268	NIS
York, NE; 2008 (RCN R080609)	40% WG	Foliar broadcast; BBCH 14, 4 leaves (~10-12" tall)	20	0.1254	--	0.1254	NIS
Payette, ID; 2008 (RCN R080610)	40% WG	Foliar broadcast; BBCH 14, 4 leaves (~10-12" tall)	30	0.1264	--	0.1264	NIS

[1] EP = End-use Product; a multiple active ingredient (MAI) water dispersible granule (WG) formulation containing 44% dicamba sodium salt (40% dicamba acid equivalents), and 17.1% diflufenzopyr sodium salt (identified as the 40% WG formulation of dicamba).
[2] RTI = Retreatment Interval.
[3] NIS = non-ionic surfactant; Induce or Preference. Ammonium sulfate liquid fertilizer was added to the spray mixture.

Primary Evaluator	Versar, Inc.	Date: 10/30/2011
Peer Reviewed and approved by	Alaa Kamel, Ph.D., RAB VII/Health Effects Division, Office of Pesticides Program	Date: 04/30/2013

Note: This DER was originally prepared under contract by Versar, Inc. (6850 Versar Center, Springfield, VA 22151; submitted 10/30/11). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

48001303 Saha, M. (2009) Method Validation of BASF Analytical Method D0902: "The Determination of Residues of Dicamba (BAS 183 H) and its Metabolite, 5-Hydroxy Dicamba in Corn Matrices using LC/MS/MS". BASF Reg. Doc. No. 2009/7003067. BASF Study Number 357998. Unpublished study prepared by BASF Corporation. 77 p.

EXECUTIVE SUMMARY:

BASF Corporation has submitted a high performance liquid chromatography method with tandem mass spectrometry detection (LC/MS/MS), BASF method D0902, for the determination of dicamba and metabolite 5-hydroxy dicamba (5-OH dicamba) in/on corn forage, kernel plus cob with husk removed (K+CWHR), and stover. The LC/MS/MS method was used for data collection in the sweet corn crop field trial study reviewed under DP# 375578 (48001305.DER. The submission includes a complete method description and validation data for corn matrices.

Briefly, homogenized samples are heated with 1 N HCl at ~90 °C for ~45 minutes. The extract is cooled to room temperature and filtered, then adjusted to volume with water. An aliquot of the extract is adjusted to pH 9-10 with concentrated NH_4OH, vortexed, and adjusted to pH 3-4 with concentrated formic acid. Sodium chloride is added, and the extract is partitioned twice with hexane:ethyl acetate (1:1, v:v) followed by centrifugation. The resulting organic phase is reduced to dryness under nitrogen, then reconstituted in methanol:water (10:90, v:v) for analysis by LC/MS/MS. The precursor/product ion transitions monitored for dicamba originated from the same ion fragment at *m/z* 218.9 and were 218.9 →174.8 and 220.9→176.8 (the isotope of *m/z* 218.9). However, two different precursor/product ion transitions were monitored for 5-OH dicamba at *m/z* 234.9→154.9 and 234.9→190.7. The first set of transitions is monitored for quantitation purposes, and the second set of transitions is monitored for confirmatory purposes.

The method includes different mobile phase gradients developed to address significant matrix interferences that were observed using the original gradient (Gradient I) for determination of dicamba in forage (monitoring ion transition at *m/z* 218.9→174.8) and for dicamba and 5-OH dicamba in stover (monitoring all transitions). Gradients I, II, IIb, and III consist of water and methanol, each containing 0.1% formic acid, and Gradient IV consists of water, containing 0.1% acetic acid and 2.5 mM dibutyl ammonium acetate, and methanol containing 1% acetic acid.

The validated limit of quantitation (LOQ; determined as the lowest level of method validation, LLMV) is 0.01 ppm for both analytes in all corn matrices. The reported limit of detection (LOD) is 0.002 ppm (~20% LOQ).

The method was adequately validated for both sets of ion transitions in samples of sweet corn forage, K+CWHR, and stover fortified with a mixed standard of dicamba and 5-OH dicamba at two concentration levels of 0.01(LOQ) and 0.10 ppm. Overall recoveries were 65-108% (average of 86% and standard deviation of 11%) for dicamba and 62-124% (average of 91% and standard deviation of 13%) for 5-OH dicamba. The fortification levels used in method validation are adequate to bracket expected residues in sweet corn matrices.

A confirmatory method was not submitted; however, monitoring a second transition ion for 5-OH dicamba constitutes a confirmatory procedure. An acceptable confirmatory ion transition for dicamba was not presented. It is noteworthy to mention that a second confirmatory ion transition for dicamba was found in the open literature in the electrospray ionization (ESI) negative ion mode at *m/z* 219→145.

No radiovalidation data were submitted; however, because the method uses acid hydrolysis procedures to release dicamba and 5-OH dicamba that are similar to those used in the enforcement analytical methods (refer to the Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger), no additional data are required.

The registrant referenced a successful independent laboratory validation (ILV) using corn grain and stover (BASF Study Number 357999; BASF Registration Document Number 2009/7000154), and stated that, although no changes to the procedure were required, minor editorial changes provided by the performing laboratory have been incorporated into the technical procedures of the method. It does not appear that this study has been submitted to the Agency; however, because ILV is not generally required for data collection methods, no additional information is required.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the analytical method test data are classified as scientifically acceptable. The analytical method is acceptable for the purpose of data collection. The acceptability of this study for regulatory purposes is addressed in the document "Supplemental Residue Field Trial Studies For Dicamba in/on Sweet Corn", D 375578, A. Kamel, 5/2013 .

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Dicamba (3,6-dichloro-2-methoxybenzoic acid) is a selective benzoic acid herbicide registered for the control of weeds prior to their emergence. Different forms of dicamba (acid and salt) have registered uses on several food/feed crops including asparagus, barley, corn (field and pop), grasses grown in pasture and rangeland, oats, proso millet, rye, sorghum, soybeans, sugarcane, and wheat. Application rates range from 0.5 to 2.8 lb ae/A. The Dicamba Reregistration Eligibility Decision (RED) was issued December 2005. The chemical structure and nomenclature of dicamba and metabolite 5-OH dicamba and the physicochemical properties of the technical grade of dicamba acid are presented in Tables A.1 and A.2.

TABLE A.1. Test Compound Nomenclature.

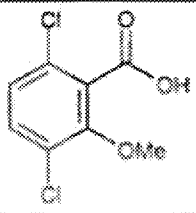
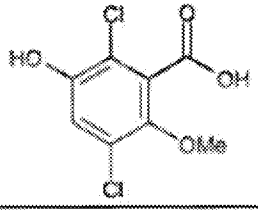
PC Code 029801	
Compound	
Common name	Dicamba
Company experimental name	BAS 183 H
IUPAC name	3,6-dichloro-o-anisic acid or 3,6-dichloro-2-methoxybenzoic acid
CAS name	3,6-dichloro-2-methoxybenzoic acid
CAS registry number	1918-00-9 (dicamba acid) or 1982-69-0 (sodium salt of dicamba)
End-use product	Not applicable
Compound	
Common name	5-Hydroxy-dicamba
Company experimental name	5-OH dicamba
IUPAC/CAS name	3,6-dichloro-5-hydroxy-2-methoxy-benzoic acid
CAS registry number	7600-50-2

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound: Dicamba.

Parameter	Value	Reference
Melting point	114-116 EC (PAI) 90-100 EC (87% TGAI)	Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger
pH	2.5-3.0 (87% TGAI)	
Density	1.57 g/mL at 25 EC (87% TGAI)	
Water solubility	0.5 g/100 mL at 25 EC (PAI)	

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound: Dicamba.		
Parameter	Value	Reference
Solvent solubility	g/100 mL at 25 EC (PAI) dioxane 118.0 ethanol 92.2 isopropyl alcohol 76.0 methylene chloride 26.0 acetone 17.0 toluene 13.0 xylene 7.8 heavy aromatic naphthalene 5.2	
Vapor pressure	3.4×10^{-5} mm Hg at 25 EC (PAI)	
Dissociation constant, pK_a	1.97 (PAI)	
Octanol/water partition coefficient, $Log(K_{OW})$	0.1 (PAI)	
UV/visible absorption spectrum	neutral: 511 (275 nm) acidic (pH 0-1): 1053 (281 nm) basic (pH 13-14): 469 (274 nm)	

B. MATERIALS AND METHODS

B.1. Data-Gathering Method

A method description and validation data have been submitted for BASF Analytical Method D0902. The LC/MS/MS method was used for data collection in the sweet corn crop field trial study reviewed under DP# 375578 (48001305.DER). The submission includes a complete method description and validation data for corn matrices. Samples of untreated sweet corn forage, K+CWHR, and stover were obtained from the sweet corn crop field trial study and were fortified with a mixed standard of dicamba and 5-OH dicamba.

A summary of the method is provided below.

B.1.1. Principle of the Method:

Samples are homogenized in the presence of dry ice and stored frozen (<-5 °C) prior to analysis.

Briefly, homogenized samples are heated with 1 N HCl at ~90 °C for ~45 minutes. The extract is cooled to room temperature and filtered, then adjusted to volume with water. An aliquot of the extract is adjusted to pH 9-10 with concentrated NH_4OH, vortexed, and adjusted to pH 3-4 with concentrated formic acid. Sodium chloride is added, and the extract is partitioned twice with hexane:ethyl acetate (1:1, v:v) followed by centrifugation. The resulting organic phase is reduced to dryness under nitrogen, then reconstituted in methanol:water (10:90, v:v) for analysis by LC/MS/MS. Two different precursor/product ion transitions were monitored for 5-OH dicamba, while both ion transitions monitored for dicamba originated from the same ion fragment..

Different mobile phase gradients of water and methanol, each containing 0.1% formic acid (Gradients I, II, IIb, and III) or water containing 0.1% acetic acid and 2.5 mM dibutyl

ammonium acetate and methanol containing 1% acetic acid (Gradient IV) were developed to address significant matrix interferences that were observed using the original gradient (Gradient I) for determination of dicamba in forage (monitoring ion transition *m/z* 218.9→174.8) and for dicamba and 5-OH dicamba in stover (monitoring all transitions). The interferences were attributed to the harsh extraction procedures, which were thought to have the potential to produce a significant matrix load, contributing to matrix interferences, subsequent signal suppression, and lack of separation of the analyte from the matrix components.

The method parameters are summarized in Table B.1.1.

TABLE B.1.1. Summary Parameters for the Analytical Method Used for the Quantitation of Dicamba and 5-OH Dicamba Residues in Corn Forage, K+CWHR, and Stover.

Method ID	BASF Analytical Method D0902
Analyte(s)	Dicamba and 5-OH dicamba
Extraction solvent/technique	Homogenized samples (5g) are heated with 1 N HCl at ~90 °C for ~45 minutes. The extract is cooled to room temperature and filtered, then adjusted to volume with water. An aliquot (5 mL) of the extract is adjusted to pH 9-10 with 0.25 mL of concentrated NH_4OH, vortexed, and adjusted to pH 3-4 with 0.2 mL of concentrated formic acid.
Cleanup strategies	Sodium chloride (2-3 g) is added, and the extract is partitioned twice with hexane:ethyl acetate (1:1, v:v; 5 mL) followed by centrifugation. The resulting organic phase is reduced to dryness under nitrogen, then reconstituted in methanol:water (10:90, v:v; 8 mL) for analysis by LC/MS/MS.
Instrument/Detector	HPLC using a Luna phenyl-hexyl column and gradient mobile phases of water and methanol, each containing 0.1% formic acid (Gradients I, II, IIB, and III) or water, containing 0.1% acetic acid and 2.5 mM dibutyl ammonium acetate, and methanol containing 1% acetic acid (Gradient IV). Tandem mass spectrometry using a PE Sciex API 4000 Biomolecular Mass Analyzer with Turbospray ionization in the negative ion mode. The precursor/product ion transitions monitored are: Dicamba: *m/z* 218.9→174.8 (quantitation) and 220.9→176.8 (confirmation) 5-OH dicamba: *m/z* 234.9→154.9 (quantitation) and 234.9→190.7 (confirmation)
Standardization method	External standardization, using mixed calibration standards (dicamba + 5-OH dicamba) prepared in methanol/water, was used to generate a standard curve through linear regression.
Stability of std solutions	Stock solutions in methanol should be made fresh every 2 months; dilutions of stock solutions should be stored refrigerated ≤1 month or according to their storage stability in a particular solvent. In addition, the stability of dicamba and 5-OH dicamba in corn extracts was determined in this study to be ≥7 and ≥8 days under refrigeration for dicamba and 5-OH dicamba, respectively.[1]
Retention times	Approximate retention times in minutes

	Dicamba	5-OH Dicamba
Gradient I (all matrices):	8.5	6.3
Gradient II (all matrices):	6.4	4.0
Gradient IIb (K+CWHR, stover):	8.3	6.0
Gradient III (forage, stover):	9.95	6.34
Gradient IV (stover, confirmatory):	NA	5.4

[1] Determined by re-analysis (re-injection) of selected method validation samples ~1 week after definitive analysis. No further results are provided herein.

B.2. Enforcement Method

Adequate enforcement methods are available for determining residues of dicamba and 5-OH dicamba in crop commodities (refer to the Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger).

C. RESULTS AND DISCUSSION

C.1. Data-Gathering Method

Method validation data for BASF method D0902 are presented in Table C.1.1. The method was adequately validated in samples of sweet corn forage, K+CWHR, and stover fortified with a mixed standard of dicamba and 5-OH dicamba at two concentration levels of 0.01 and 0.10 ppm. Overall recoveries were 65-108% (average of 86% and standard deviation of 11%) for dicamba and 62-124% (average of 91% and standard deviation of 13%) for 5-OH dicamba. The fortification levels used in method validation are adequate to bracket expected residues in sweet corn matrices. Method validation was conducted at BASF Agricultural Research Center (Research Triangle Park, NC).

The method characteristics for BASF method D0902 are summarized in Table C.1.2. The validated limit of quantitation (LOQ; determined as the LLMV) is 0.01 ppm for both analytes in all corn matrices. The reported limit of detection (LOD) is 0.002 ppm (~20% LOQ).

No confirmatory method was submitted; however, monitoring a second transition ion for each analyte constitutes confirmatory procedures for the method.

No radiovalidation data were submitted; however, because the method uses acid hydrolysis procedures to release dicamba and 5-OH dicamba that are similar to those used in the enforcement analytical methods (refer to the Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger), no additional data are required.

TABLE C.1.1. Recovery Results from Method Validation of Corn Forage, K+CWHR, and Stover using the Data Gathering Analytical Method. Standards were Prepared in Methanol.

Matrix	Mobile Phase Gradient[1]	Spiking Level (ppm)	Quantitation[2]		Confirmation[3]	
			Recoveries Obtained (%)	Mean Recovery ± Std. Dev. [CV] (%)	Recoveries Obtained (%)	Mean Recovery ± Std. Dev. [CV] (%) CV
Dicamba						
Forage	I	0.01	NR/NC[4]	NR/NC	82, 88, 83, 74, 77	81 ± 6 [7]
	III		100, 97, 99, 97, 103	99 ± 3 [3]	85, 91, 90, 101, 95	92 ± 6 [7]
	I	0.10	NR/NC	NR/NC	95, 82, 81, 77, 75	82 ± 8 [9]
	III		105, 108, 103, 99, 102	103 ± 3 [3]	98, 101, 105, 94, 103	100 ± 5 [5]
K+CWHR	I	0.01	80, 86, 89, 78, 79	82 ± 5 [6]	90, 94, 89, 96, 75	89 ± 8 [9]
		0.10	80, 85, 85, 77, 86	83 ± 4 [5]	90, 92, 74, 88, 90	87 ± 7 [8]
Stover	IIB	0.01	65, 69, 79, 65, 69	69 ± 6 [8]	NR/NC	NR/NC
		0.10	72, 82, 86, 85, 74	80 ± 6 [8]	NR/NC	NR/NC
	III	0.01	NR/NC	NR/NC	79[5], 76[5], 84, 80, 80	80 ± 3 [4]
		0.10	NR/NC	NR/NC	85, 88, 93, 69, 75	82 ± 10 [12]

TABLE C.1.1. Recovery Results from Method Validation of Corn Forage, K+CWHR, and Stover using the Data Gathering Analytical Method. Standards were Prepared in Methanol.

Matrix	Mobile Phase Gradient[1]	Spiking Level (ppm)	Quantitation[2]		Confirmation[3]	
			Recoveries Obtained (%)	Mean Recovery ± Std. Dev. [CV] (%)	Recoveries Obtained (%)	Mean Recovery ± Std. Dev. [CV] (%) CV
5-OH Dicamba						
Forage	I	0.01	79, 73, 86, 74, 73	77 ± 6 [8]	82, 86, 88, 84, 86	85 ± 2 [3]
	III[6]		91, 89, 80, 96, 74	86 ± 9 [10]	102, 110, 85, 89, 92	96 ± 10 [11]
	I	0.10	99, 91, 100, 99, 92	96 ± 4 [5]	89, 102, 94, 100, 100	97 ± 6 [6]
	III[6]		101, 99, 104, 105, 110	104 ± 4 [4]	91, 89, 115, 124, 89	102 ± 17 [16]
K+CWHR	I	0.01	76, 70, 87, 90, 73	79 ± 9 [11]	105, 115, 82, 114, 98	103 ± 13 [13]
		0.10	106, 86, 103, 94, 107	99 ± 9 [9]	92, 99, 101, 86, 84	93 ± 8 [8]
Stover	IIB	0.01	76, 71, 65, 82, 81	75 ± 7 [9]	NR/NC	NR/NC
			NR/NC	NR/NC	80[5], 62[5], 75, 70, 70	71 ± 6 [9]
	IV	0.10	81, 87, 101, 102, 93	93 ± 9 [10]	NR/NC	NR/NC
			NR/NC	NR/NC	108, 106, 91, 76, 102	96 ± 13 [14]

[1] Gradients I, II, IIB, and III are water and methanol, each containing 0.1% formic acid; Gradient IV is water containing 0.1% acetic acid and 2.5 mM dibutyl ammonium acetate and methanol containing 1% acetic acid.
[2] Monitored ion transitions were *m/z* 218.9→174.8 for dicamba and 234.9→154.9 for 5-OH dicamba.
[3] Monitored ion transitions were *m/z* 220.9→176.8 for dicamba and 234.9→190.7 for 5-OH dicamba.
[4] NR/NC = Not reported or not conducted.
[5] Mean of replicate analyses.
[6] The gradient for this data set was incorrectly identified as Gradient I in Tables 1 and 2 of the MRID; the raw data indicate that the gradient used was actually Gradient III (pp. 50 and 51).

TABLE C.1.2. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Dicamba and 5-OH Dicamba Residues in Corn Forage, K+CWHR, and Stover.

Analyte(s)	Dicamba and 5-OH dicamba
Equipment ID	Shimadzu UFLC HPLC system connected to a PE Sciex API 4000 Mass Analyzer with Turbospray ionization (negative) mode
Limit of quantitation (LOQ)	The LOQ, determined as the LLMV, was 0.01 ppm for both analytes in all matrices.
Limit of detection (LOD)	The LOD was 0.002 ppm (~20% LOQ) for both analytes in all matrices.
Accuracy/Precision	Percent recoveries and coefficients of variance (CVs) indicate acceptable accuracy/precision at 0.01-0.10 ppm for all analytes and all matrices. Average recoveries (and CVs) were 86% (12%) for dicamba and 91% (14%) for 5-OH dicamba. See Table C.1.2 above.
Reliability of the Method/ [ILV]	The registrant indicated that an ILV was conducted (BASF Study Number 357999; BASF Registration Document Number 2009/7000154). This study does not appear to have been submitted to the Agency; however, the registrant stated that the ILV using corn grain and stover was successful and that no changes were required to the procedure.
Linearity	The method/detector response was linear (coefficient of determination, r^2> 0.9996 for dicamba and r^2> 0.9997 for5-OH dicamba) and within the range of 0.1-2.5 ng/mL.
Specificity	The control chromatograms generally have no peaks above the chromatographic background, and the spiked sample chromatograms contain only the analyte peak of interest. Peaks were well defined and symmetrical. There appeared to be no carryover to the following chromatograms.

C.2. Enforcement Method

Adequate enforcement methods are available for determining residues of dicamba and 5-OH dicamba in crop commodities (refer to the Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger).

C.3. Independent Laboratory Validation

The registrant referenced a successful independent laboratory validation (ILV) using corn grain and stover (BASF Study Number 357999; BASF Registration Document Number 2009/7000154), and stated that, although no changes to the procedure were required, minor editorial changes provided by the performing laboratory have been incorporated into the technical procedures of the method. It does not appear that this study has been submitted to the Agency; however, because ILV is not generally required for data collection methods, no additional information is required.

D. CONCLUSION

The LC/MS/MS method used for data collection in the sweet corn crop field trials reviewed under DP# 375578 (refer to 48001305.DER) adequately determines residues of dicamba and 5-OH dicamba in corn forage, K+CWHR, and stover. Acceptable method validation data were submitted reflecting both the quantitative and confirmatory ion transitions monitored for determination of dicamba and 5-OH dicamba, and the fortification levels used in method validation are adequate to bracket expected residues in sweet corn matrices.

E. REFERENCES

DP#:	317699
Subject:	Dicamba. Residue Chemistry Considerations for the Reregistration Eligibility Decision (RED) Document. Summary of Analytical Chemistry and Residue Data.
From:	C. Olinger
To:	K. Tyler
Dated:	12/20/05
MRID(s):	None

F. DOCUMENT TRACKING

RDI:
Petition Number(s):
DP Barcode(s): D375578
PC Code: 029801

Template Version September 2003

Primary Evaluator	Versar, Inc.	Date: 10/30/2011
Peer Reviewed and approved by	Alaa Kamel, Ph.D., RAB VII/Health Effects Division, Office of Pesticides Program	Date: 04/30/2013

Note: This Data Evaluation Record (DER) was originally prepared under contract by Versar, Inc. (6850 Versar Center, Springfield, VA 22151; submitted 10/30/11). The DER has been reviewed by HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

48001304 Perez, R., Perez, S., and Tarkalanov, N. (2010) Evaluation of 5-OH-Dicamba and 3,6-Dichlorosalicylic ACID (DCSA) FDA Multiresidue Method (MRM) Testing: Lab Project No.: ADPEN-2K9-0508BAS. Study No.: 357203. Unpublished study prepared by BASF Corporation. 247 p.

EXECUTIVE SUMMARY:

In response to the Data Call In (DCI) for the Dicamba RED to support the reregistration of the herbicide dicamba (GDCI-29801-27682), BASF Corporation has submitted multiresidue testing data for the dicamba metabolites of concern [3,6-dichloro-5-hydroxy benzoic acid (5-OH dicamba) and 3,6-dichlorosalicylic acid (DCSA)]. The metabolites were screened through multiresidue methods described in the United States Food and Drug Administration (FDA) Pesticide Analytical Manual Volume I (PAM Vol. I). 5-OH dicamba was tested through Protocols A, B, C, D, E and F. DCSA was tested through Protocols A, B, and C. DCSA was not tested under Protocol D, E, or F because it did not show acceptable chromatographic separation (yielded multiple peaks) under Protocol C. 5-OH dicamba and DCSA were not tested under Protocol G because the compounds are not a substituted urea. The study was conducted by ADPEN Laboratories, Inc. (Jacksonville, FL).

5-OH dicamba and DCSA were tested for natural fluorescence using procedures outlined in Protocol A; however, testing was suspended because of the lack of a fluorescence response at the excitation and emission wavelengths.

Protocol B testing of 5-OH dicamba and DCSA indicated both could be methylated; however, only DCSA was successful through the complete method with partial recovery in soybean forage fortified at 0.05 and 0.5 ppm (53.2-61.1% and 38.5-45.7%, respectively). Based on these results Protocol B may be applicable for analysis of DCSA on non-fatty food.

Protocol C testing of the compounds indicated that further testing using Protocol D, E, and F was required for 5-OH dicamba; this compound was found to show acceptable chromatographic separation with sufficient response on tested modules DG13. DCSA did not show acceptable

chromatographic separation (yielded multiple peaks) on both modules tested under Protocol C; therefore, no further testing was conducted.

5-OH dicamba was found to be unrecoverable through both cleanup tests when tested under Protocols D, E, and F; therefore, further testing under these Protocols was not conducted.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the multiresidue method testing data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in D 375578, A. Kamel, 6/11/2013.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided.

A. BACKGROUND INFORMATION

Dicamba (3,6-dichloro-2-methoxybenzoic acid) is a selective benzoic acid herbicide registered for the control of weeds prior to their emergence. Different forms of dicamba (acid and salt) have registered uses on several food/feed crops including asparagus, barley, corn (field and pop), grasses grown in pasture and rangeland, oats, proso millet, rye, sorghum, soybeans, sugarcane, and wheat. Application rates range from 0.5 to 2.8 lb ae/A. The Dicamba Reregistration Eligibility Decision (RED) was issued December 2005. The chemical structure and nomenclature of dicamba and its metabolites 5-OH dicamba and DCSA and the physicochemical properties of the technical grade of dicamba acid are presented in Tables A.1 and A.2.

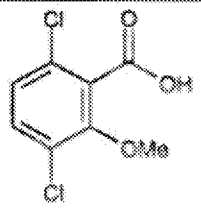
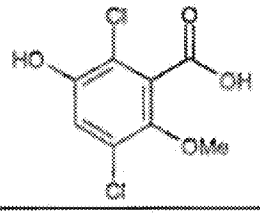
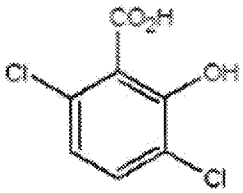
TABLE A.1. Test Compound Nomenclature.	
PC Code 029801	
Compound	
Common name	Dicamba
Company experimental name	BAS 183 H
IUPAC name	3,6-dichloro-o-anisic acid or 3,6-dichloro-2-methoxybenzoic acid
CAS name	3,6-dichloro-2-methoxybenzoic acid
CAS registry number	1918-00-9 (dicamba acid) or 1982-69-0 (sodium salt of dicamba)
Compound	
Common name	5-Hydroxy-dicamba
Company experimental name	5-OH dicamba
IUPAC/CAS name	3,6-dichloro-5-hydroxy-2-methoxy-benzoic acid
CAS registry number	7600-50-2
Compound	
Common name	3,6-dichlorosalicylic acid
Company experimental name	DCSA
IUPAC/CAS name	
CAS registry number	3401-80-7

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound: Dicamba.		
Parameter	Value	Reference
Melting point	114-116 °C (PAI) 90-100 °C (87% TGAI)	Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger
pH	2.5-3.0 (87% TGAI)	
Density	1.57 g/mL at 25 °C (87% TGAI)	
Water solubility	0.5 g/100 mL at 25 °C (PAI)	
Solvent solubility	g/100 mL at 25 °C (PAI) dioxane 118.0 ethanol 92.2 isopropyl alcohol 76.0 methylene chloride 26.0 acetone 17.0 toluene 13.0 xylene 7.8 heavy aromatic naphthalene 5.2	
Vapor pressure	3.4×10^{-5} mm Hg at 25 °C (PAI)	
Dissociation constant, pK_a	1.97 (PAI)	
Octanol/water partition coefficient, $Log(K_{OW})$	0.1 (PAI)	
UV/visible absorption spectrum	neutral: 511 (275 nm) acidic (pH 0-1): 1053 (281 nm) basic (pH 13-14): 469 (274 nm)	

B. MATERIALS AND METHODS

5-OH dicamba and DCSA were tested for natural fluorescence using procedures outlined in Protocol A. 5-OH dicamba and DCSA were not tested under Protocol G because the compounds are not a substituted urea. Both 5-OH dicamba and DCSA were methylated according to Protocol B. Protocol C testing was performed to determine the appropriate module for use in the analysis of the test substances with Protocols D, E and F. Under Protocol C, modules DG1 (ECD detector with Equity-1 column) and DG13 (ECD detector with DB-17 column) were selected for evaluation of 5-OH dicamba and DCSA due to their specificity for compounds containing a halogen atom. Because 5-OH dicamba showed acceptable chromatographic separation under DG13 with ECD, testing was conducted under Protocol D for recovery through Florisil. 5-OH dicamba was tested under Protocol E and F for recovery through Florisil using procedures C1 and C2.

C. RESULTS AND DISCUSSION

The results of the multiresidue method testing are presented in Table C.1 below.

Testing through Protocol A for both substances was suspended due to the lack of a fluorescence response at the excitation and emission wavelengths of 288 and 330 nm.

Under Protocol B testing, DCSA was successful through the complete method with partial recovery in soybean forage fortified at 0.05 and 0.5 ppm (53.2-61.1% and 38.5-45.7%,

respectively); 5-OH dicamba recoveries were ≤6.0% at both of the fortification levels on soybean forage. Recoveries of 5-OH-Dicamba and DCSA in soybean seed were low for all fortification levels at 0% and ≤3.4%, respectively. Based on these results Protocol B may be applicable for analysis of DCSA on non-fatty food.

Protocol C testing of 5-OH-Dicamba indicated that further testing using Protocols D, E, and F was required. The Protocol C results indicated that the ECD (with a DB-17 column) was the most appropriate detector for the test substance.

Under Protocol D, the recovery of the test substances through the Florisil column cleanup procedures was evaluated first because the ECD was found to be the most suitable detector for 5-OH dicamba. 5-OH dicamba was not recoverable from the Florisil column cleanup procedures.

Testing of 5-OH dicamba through Protocols E and F was also not recoverable from the Florisil column cleanup procedures.

TABLE C.1. Results of Multiresidue Methods Testing with Dicamba Metabolites (5-OH dicamba and DCSA).

PAM I Protocol	Analyte	Results	Comments
A	5-OH-dicamba 3,6-dichlorosalicylic acid (DCSA)	Subjected to testing under Module DL2 and neither compound fluoresced at excitation and emission wavelengths of 288 and 330 nm.	Protocol A is not applicable for analysis of 5-OH dicamba and DCSA.
B	5-OH-dicamba	Methylated according to Protocol B and was found to produce a signal under Module DG1. Acceptable recovery was found for both the GPC and Florisil cleanups, however, recoveries through the complete method on both non-fatty food (soybean forage) and fatty food (soybean seeds) were low (≤6%) or zero.	Protocol B is not applicable for analysis of 5-OH dicamba.
	DCSA	Methylated according to Protocol B and was found to produce a signal under Module DG1. Acceptable recovery was found for both the GPC and Florisil cleanups. Recoveries through the complete method on non-fatty food (soybean forage) were 38.3-61.1%, however, recoveries for fatty food (soybean seeds) were low at 0-3.4%.	Partial recoveries were obtained for DCSA in soybean forage fortified at 0.05 and 0.5 ppm. Based on these results Protocol B may be applicable for analysis of DCSA on non-fatty food.

TABLE C.1. Results of Multiresidue Methods Testing with Dicamba Metabolites (5-OH dicamba and DCSA).

PAM I Protocol	Analyte	Results	Comments
C	5-OH dicamba	Subjected to testing under Section 302, using modules DG-1 (electron capture detection; ECD with Equity-1 column) and DG-13 (ECD with DB-17 column). In module DG-1, the instrument produced multiple inconsistent peaks indicating thermal degradation. In module DG-13, 50% full-scale deflection (FSD) was achieved at a concentration of 1.24 ng with a relative retention time (rrt; chlorpyrifos) of 0.66 minutes.	Based on the results of Protocol C testing, further testing through Protocols D, E, and F was required. The results indicated that the best detector for 5-OH dicamba is the ECD.
	DCSA	Subjected to testing under Section 302, using modules DG-1 (ECD with Equity-1 column) and DG-13 (ECD with DB-17 column). In module DG-1 and DG-13, the instrument produced multiple inconsistent peaks indicating thermal degradation.	Protocol C is not applicable for analysis of DCSA.
D	5-OH dicamba	Because 5-OH-Dicamba was chromatographable in Protocol C testing with ECD, recovery through Florisil was investigated. Recoveries through both cleanup tests, Section 302 C1 and Section 302 C5, were 0%. No further testing was conducted.	Protocol D is not applicable for analysis of 5-OH dicamba.
	DCSA	Not tested.	
E	5-OH dicamba	Because 5-OH-Dicamba was chromatographable in Protocol C testing with ECD, recovery through Florisil was investigated. Recoveries through both cleanup tests, Section 303 C1 and Section 303 C2, were 0%. No further testing was conducted.	Protocol E is not applicable for analysis of 5-OH dicamba.
	DCSA	Not tested.	
F	5-OH dicamba	The Florisil cleanup test in Protocols E (Sec. 303 C1 and C2) and F (Sec. 304 C1 and C2) are identical. Only one test was done for both. No further testing was conducted.	Protocol F is not applicable for analysis of 5-OH dicamba.
	DCSA	Not tested.	
G	5-OH dicamba	Not tested.	Test substances are not a substituted urea.
	DCSA		

D. CONCLUSION

The metabolites of dicamba, 5-OH dicamba and DCSA were adequately evaluated for recovery through FDA multiresidue methods. Because the test substances are not substituted ureas, testing under Protocol G was not conducted. Testing through Protocol A was conducted for both substances; however, testing was suspended due to the lack of a fluorescence response at the excitation and emission wavelengths of 288 and 330 nm. Under Protocol B testing, DCSA was successful through the complete method with partial recovery in soybean forage fortified at 0.05 and 0.5 ppm. Protocol B described in PAM Vol. I may be applicable for determination of DCSA on non-fatty food. Protocol C testing of 5-OH dicamba indicated that further testing using

Protocols D, E, and F was required. Because the detector determined to be most appropriate for the test compounds was the ECD, the recovery of the compounds through the Florisil column cleanup procedures was evaluated first under Protocol D. 5-OH dicamba was not recoverable from the Florisil column cleanup procedures under Protocols D, E, and F.

E. REFERENCES

DP#: 317699
Subject: Dicamba. Residue Chemistry Considerations for the Reregistration Eligibility Decision (RED) Document. Summary of Analytical Chemistry and Residue Data.
From: C. Olinger
To: K. Tyler
Dated: 12/20/05
MRID(s): None

F. DOCUMENT TRACKING

RDI:
Petition Number(s):
DP Barcode(s): D375578
PC Code: 029801

Template Version June 2005

Primary Evaluator	Versar, Inc	Date: 10/30/2011
Peer Reviewed and Approved by	Alaa Kamel, Ph.D., RAB VII/Health Effects Division, Office of Pesticides Program	Date: 5/8/2013

Note: This DER was originally prepared under contract by Versar, Inc. (6850 Versar Center, Springfield, VA 22151; submitted 10/30/11). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

48001305 White, M. (2009) Magnitude of Dicamba Residues in Sweet Corn Following an Application of BAS 799 00 H (Status®). BASF Reg. Doc. No. 2009/7003026. BASF Study Number: 351572. Unpublished study prepared by BASF Corporation. 79 p.

EXECUTIVE SUMMARY:

BASF has submitted crop field trial for dicamba on sweet corn. The data were submitted in response to an Agency memorandum (DP# 275611, 7/26/01, G. Kramer) of an Interregional Research Project No. 4 (IR-4) petition for uses of dicamba on sweet corn. Three field trials were conducted in the United States during the 2008 growing season in the North American Free Trade Agreement (NAFTA) Zones 1 (NY; 1 trial), 5 (NE; 1 trial), and 11 (ID; 1 trial).

Each trial consisted of one untreated plot and one treated plot. All treatment applications were made using a multiple active ingredient (MAI) water dispersible granule (WG) formulation containing 44% dicamba sodium salt (40% dicamba acid equivalents), and 17.1% diflufenzopyr sodium salt (identified as the 40% WG formulation of dicamba) and isoxadifen-ethyl. The samples were neither analyzed for diflufenzopyr nor for isoxadifen-ethyl. At each trial location, dicamba was applied at 0.125-0.127 lb acid equivalent (ae)/A. Applications were made using boom sprayer ground equipment in spray volumes of 20-40 gal/A. A non-ionic surfactant (NIS) mixed with an ammonium sulfate liquid fertilizer was added to each spray mixture.

Samples of corn forage and sweet corn kernel plus cob with husks removed (K+CWHR) were harvested from all trials at pre-harvest intervals (PHI) of 32-33 and 53-72 days and stover samples were harvested at PHIs of 72 and 88-98 days. The K+CWHR and stover samples taken at the first sampling interval were generally immature; however, those taken at the last sampling interval were commercially acceptable RAC samples.

Sweet corn samples were analyzed for residues of dicamba and its metabolite 5-OH dicamba using High Pressure Liquid Chromatography -Tandem Mass Spectrometry (LC/MS/MS); Method D0902. The limit of quantitation (LOQ; determined as the lowest limit of method validation, LLMV) was 0.01 ppm for all analytes in all sweet corn matrices. The method was verified prior to and in conjunction with sample analysis and is considered adequate based on

acceptable method validation and concurrent recovery data. The fortification levels used in concurrent method recovery were adequate to bracket expected residue levels. The concurrent recoveries reported in this document were not corrected for residues in controls (residues in controls <LOQ).

Samples were stored frozen (<-5 °C) from collection to analysis for 175-242 days (5.8-8.0 months) for forage, 156-199 days (5.1-6.5 months) for stover, and 178-244 days (5.9-8.0 months) for K+CWHR. Samples were analyzed within 0-3 days of extraction. Adequate storage stability data are available to support the study reflecting the stability of residues of dicamba and 5-OH dicamba under frozen storage conditions in/on field corn forage, silage, grain, and fodder for up to 3 and 2 years, respectively (refer to the Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger). These data are acceptable to support the storage conditions and durations of samples from the submitted field trials.

Following one foliar broadcast application of the 40% WG formulation of dicamba at a total rate of 0.125-0.127 lb ae/A, combined residues of dicamba and its metabolite 5-OH dicamba (and per trial averages) were <0.02-0.0886 ppm (<0.02-0.0782 ppm) and <0.02-0.0688 ppm (<0.02-0.0679 ppm) in/on forage at 32-33 and 53-72-day PHIs, respectively. Combined residues of dicamba and 5-OH dicamba (and per trial averages) were <0.02-0.0451 ppm (<0.02-0.0393 ppm) and <0.02-0.0525 ppm (<0.02-0.0416 ppm) in/on stover at 72 and 88-98-day PHIs, respectively. Combined residues of dicamba and 5-OH dicamba were below the LOQ (<0.02 ppm) in/on all samples of K+CWHR at 32-33 and 53-72-day PHIs.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the U.S. EPA Residue Chemistry Summary Document [D 375578, A. Kamel 6/11/2013].

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance, and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Dicamba (3,6-dichloro-2-methoxybenzoic acid) is a selective benzoic acid herbicide registered for the control of weeds prior to their emergence. Different forms of dicamba (acid and salt) have registered uses on several food/feed crops including asparagus, barley, corn (field and pop), grasses grown in pasture and rangeland, oats, proso millet, rye, sorghum, soybeans, sugarcane, and wheat. Application rates range from 0.5 to 2.8 lb ae/A. The Dicamba Reregistration Eligibility Decision (RED) was issued December 20, 2005. The chemical structure and

nomenclature of dicamba and metabolite 5-OH dicamba and the physicochemical properties of the technical grade of dicamba acid are presented in Tables A.1 and A.2.

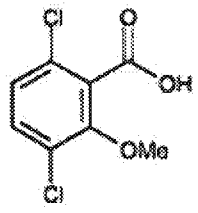
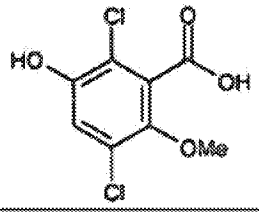
TABLE A.1. Test Compound Nomenclature.	
PC Code 029801	
Compound	
Common name	Dicamba
Company experimental name	BAS 183 H
IUPAC name	3,6-dichloro-o-anisic acid or 3,6-dichloro-2-methoxybenzoic acid
CAS name	3,6-dichloro-2-methoxybenzoic acid
CAS registry number	1918-00-9 (dicamba acid) or 1982-69-0 (sodium salt of dicamba)
End-use product	40% WG formulation (Status® Herbicide; MAI formulation containing 44% dicamba sodium salt and 17.1% diflufenzopyr sodium salt)
Compound	
Common name	5-Hydroxy-dicamba
Company experimental name	5-OH dicamba
IUPAC/CAS name	3,6-dichloro-5-hydroxy-2-methoxy-benzoic acid
CAS registry number	7600-50-2

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound: Dicamba.		
Parameter	Value	Reference
Melting point	114-116 °C (PAI) 90-100 °C (87% TGAI)	Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger
pH	2.5-3.0 (87% TGAI)	
Density	1.57 g/mL at 25 °C (87% TGAI)	
Water solubility	0.5 g/100 mL at 25 °C (PAI)	
Solvent solubility	g/100 mL at 25 °C (PAI) dioxane 118.0 ethanol 92.2 isopropyl alcohol 76.0 methylene chloride 26.0 acetone 17.0 toluene 13.0 xylene 7.8 heavy aromatic naphthalene 5.2	
Vapor pressure	3.4×10^{-5} mm Hg at 25 °C (PAI)	
Dissociation constant, pK_a	1.97 (PAI)	
Octanol/water partition coefficient, $Log(K_{OW})$	0.1 (PAI)	
UV/visible absorption spectrum	neutral: 511 (275 nm) acidic (pH 0-1): 1053 (281 nm) basic (pH 13-14): 469 (274 nm)	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Three sweet corn field trials were conducted in the United States during the 2008 growing season in NAFTA Growing Zones 1 (NY; 1 trial), 5 (NE; 1 trial), and 11 (ID; 1 trial).

Each trial consisted of one untreated plot and one treated plot. All treatment applications were made using a MAI WG formulation containing 44% dicamba sodium salt (40% dicamba acid equivalents), and 17.1% diflufenzopyr sodium salt (identified as the 40% WG formulation of dicamba). The samples were not analyzed for diflufenzopyr. At each trial location, dicamba was applied at 0.125-0.127 lb ae/A. Applications were made using boom sprayer ground equipment in spray volumes of 20-40 gal/A. A NIS mixed with an ammonium sulfate liquid fertilizer was added to each spray mixture.

Samples of corn forage and sweet corn K+CWHR were harvested from all trials at PHIs of 32-33 and 53-72 days and stover samples were harvested at PHIs of 72 and 88-98 days. The K+CWHR and stover samples taken at the first sampling interval were generally immature; however, those taken at the last sampling interval were commercially acceptable RAC samples.

Common cultural practices were followed to maintain the crop, and additional maintenance pesticides and fertilizers were used at the sites to produce a commercial quality crop. Weather data were not presented. The registrant indicated that precipitation was below normal in June, August, and September and above normal in July and October at the NY trial site. At the NE

trial site, August was cooler than normal; precipitation was above normal in June and July and below normal in August. Precipitation was slightly less than normal during the trial period at the ID trial site. Irrigation was used to supplement rainfall as needed.

Trial conditions are presented in Table B.1.1. The study use pattern is presented in Table B.1.2, and the crop varieties grown are identified in Table C.3.

TABLE B.1.1 Trial Site Conditions.

Trial Identification: County, State; Year (Trial No.)	Soil characteristics			
	Type	%OM[1]	pH[1]	CEC[1] meq/100 g
Wayne, NY; 2008 (RCN R080608)	Silt loam	4.7	5.8	8.2
York, NE; 2008 (RCN R080609)	Silty clay loam	2.5	6.3	20.1
Payette, ID; 2008 (RCN R080610)	Loam	1.97	8.1	NR

NR= Not reported
[1]These parameters are optional except in cases where their value affects the use pattern for the chemical.

TABLE B.1.2. Study Use Pattern.

Location County, State; Year (Trial ID)	EP[1]	Application					Tank Mix/ Adjuvants[3]
		Method; Timing	Volume gal/A	Rate (lb ae/A)	RTI[2] (days)	Total Rate (lb ae/A)	
Wayne, NY; 2008 (RCN R080608)	40% WG	Foliar broadcast; BBCH 15, 5 leaves (~10-12" tall)	40	0.1268	--	0.1268	NIS
York, NE; 2008 (RCN R080609)	40% WG	Foliar broadcast; BBCH 14, 4 leaves (~10-12" tall)	20	0.1254	--	0.1254	NIS
Payette, ID; 2008 (RCN R080610)	40% WG	Foliar broadcast; BBCH 14, 4 leaves (~10-12" tall)	30	0.1264	--	0.1264	NIS

[1] EP = End-use Product; a multiple active ingredient (MAI) water dispersible granule (WG) formulation containing 44% dicamba sodium salt (40% dicamba acid equivalents), and 17.1% diflufenzopyr sodium salt (identified as the 40% WG formulation of dicamba).
[2] RTI = Retreatment Interval.
[3] NIS = non-ionic surfactant; Induce or Preference. Ammonium sulfate liquid fertilizer was added to the spray mixture.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Regions	Sweet Corn		
	Submitted	Requested[1]	
		Canada	U.S.
1	1	--	2/1
1A	--	--	--
2	--	--	1/1
3	--	--	1/1
4	--	--	--
5	1	--	5/3
5A	--	--	--
5B	--	--	--
6	--	--	--
7	--	--	--
7A	--	--	--
8	--	--	--
9	--	--	--
10	--	--	1/1
11	1	--	1/1
12	--	--	1/1
13	--	--	--
14	--	--	--
15	--	--	--
16	--	--	--
17	--	--	--
18	--	--	--
19	--	--	--
20	--	--	--
21	--	--	--
Total	3[2]	--	12/9

[1] As per Table 5 of 860.1500 for sweet corn; the second number reflects a 25% reduction in the number of field trials allowed for the crop as a representative commodity in support of a crop group/subgroup tolerance or when application results in no quantifiable residues.

[2] The registrant indicated that this study is providing bridging data to supplement previously submitted residue data for dicamba on corn; therefore, only three trials were submitted.

B.2. Sample Handling and Preparation

At all test sites, single control and duplicate treated sweet corn forage and K+CWHR samples were harvested at the beginning of pollen shedding to milk growth stage (32-33-day PHI) and at the milk to late dough growth stage (53-72-day PHI). Stover samples were harvested at the early dough to fully ripe stage (72-day PHI) and BBCH 93 to senescence (88-98-day PHI). The K+CWHR and stover samples taken at the first sampling interval were generally immature; however, those taken at the last sampling interval were commercially acceptable RAC samples. The separate forage and stover samples (≥12 plants) were recombined (if needed) to reduce the gross sample weight. All treated samples were placed in frozen storage at the field trials

promptly after collection (time not reported). All samples were shipped within 1-62 days of collection by freezer truck to the analytical laboratory, BASF Agricultural Research Center (Research Triangle Park, NC) for residue analysis. Samples were maintained frozen (<-5 °C) at the analytical laboratory prior to homogenization and analysis. In preparation for analysis, samples were homogenized using a Stephan floor chopper in the presence of dry ice.

B.3. Analytical Methodology

Samples of sweet corn (forage, stover, and K+CWHR) were analyzed for residues of dicamba and 5-OH dicamba using LC-MS/MS method D0902. A brief description of the method was included in the submission; for a complete description and method validation refer to 48001303.DER.

Briefly, homogenized samples were heated with 1 N HCl at ~90 °C for ~45 minutes. The extract was cooled to room temperature and filtered, then adjusted to volume with water. The extract was adjusted to pH 9-10 with concentrated NH_4OH, vortexed, and adjusted to pH 3-4 with concentrated formic acid. Sodium chloride was added, and the extract was partitioned twice with hexane:ethyl acetate (1:1, v:v) followed by centrifugation. The resulting organic phase was reduced to dryness under nitrogen, then reconstituted in methanol:water (10:90, v:v) for analysis by LC/MS/MS. Two transition ions were monitored for each analyte.

The LOQ (determined as the LLMV), was 0.01 ppm for all analytes in the corn matrices; the corresponding limit of detection (LOD) was 0.002 ppm.

The method was validated prior to and in conjunction with the analysis of the field trial samples.

C. RESULTS AND DISCUSSION

Sample storage conditions and durations are summarized in Table C.2. Samples were stored frozen (<-5 °C) from collection to analysis for 175-242 days (5.8-8.0 months) for forage, 156-199 days (5.1-6.5 months) for stover, and 178-244 days (5.9-8.0 months) for K+CWHR. Samples were analyzed within 0-3 days of extraction. Adequate storage stability data are available to support the study reflecting the stability of residues of dicamba and 5-OH dicamba under frozen storage conditions in/on field corn forage, silage, grain, and fodder for up to 3 and 2 years, respectively (refer to the Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger). These data are acceptable to support the storage conditions and durations of samples from the submitted field trials.

Concurrent method recovery data for the LC/MS/MS method are presented in Table C.1. For concurrent method recovery, sweet corn samples were fortified at 0.01-1.0 ppm with dicamba and 5-OH dicamba. Average recoveries were within the acceptable range of 70-120%. The method is considered adequate based on acceptable method validation (48001303.DER) and concurrent method validation. The fortification levels used in concurrent method recovery were adequate to bracket expected residue levels.

Apparent residues of dicamba and 5-OH dicamba were below the LOQ in/on all samples of untreated sweet corn forage, stover, and K+CWHR. The concurrent recoveries reported in this document were not corrected for residues in controls (residues in controls <LOQ).

Residue data from the sweet corn trials are presented in Table C.3, and a summary of the residue data is presented in Table C.4. Following one foliar broadcast application of the 40% WG formulation of dicamba at a total rate of 0.125-0.127 lb ae/A, combined residues of dicamba and its metabolite 5-OH dicamba (and per trial averages) were <0.02-0.0886 ppm (<0.02-0.0782 ppm) and <0.02-0.0688 ppm (<0.02-0.0679 ppm) in/on forage at 32-33 and 53-72-day PHIs, respectively. Combined residues of dicamba and 5-OH dicamba (and per trial averages) were <0.02-0.0451 ppm (<0.02-0.0393 ppm) and <0.02-0.0525 ppm (<0.02-0.0416 ppm) in/on stover at 72 and 88-98-day PHIs, respectively. Combined residues of dicamba and 5-OH dicamba were below the LOQ (<0.02 ppm) in/on all samples of K+CWHR at 32-33 and 53-72-day PHIs.

TABLE C.1. Summary of Concurrent Recoveries of Dicamba and its Metabolite 5-OH Dicamba from Sweet Corn.

Matrix	Analyte	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean ± Std. Dev. (%)[1]
Forage	Dicamba	0.01	2	80, 88	84
		1.0	2	97, 98	97
	5-OH Dicamba	0.01	2	97, 96	97
		1.0	2	104, 103	104
K+CWHR	Dicamba	0.01	1	88[2]	88
		1.0	1	100[2]	100
	5-OH Dicamba	0.01	1	96[2]	96
		1.0	1	110[2]	110
Stover	Dicamba	0.01	1	75	75
		1.0	1	96	96
	5-OH Dicamba	0.01	1	87	87
		1.0	1	98	98

[1] Standard deviation is not calculated for sample sizes <3.
[2] Mean of several injections of the same fortification sample.

TABLE C.2. Summary of Storage Conditions.

Matrix	Analyte	Storage Temperature (°C)	Actual Storage Duration[1]	Limit of Demonstrated Storage Stability[2]
Forage	Dicamba	<-5	175-242 days (5.8-8.0 months)	Residues of dicamba and 5-OH dicamba are stable under frozen storage conditions in/on field corn forage, silage, grain, and fodder for up to 3 and 2 years, respectively.
	5-OH Dicamba			
K+CWHR	Dicamba	<-5	178-244 days (5.9-8.0 months)	
	5-OH Dicamba			
Stover	Dicamba	<-5	156-199 days (5.1-6.5 months)	
	5-OH Dicamba			

[1] Interval from harvest to analysis. Samples were analyzed within 0-3 days of extraction.
[2] Refer to the Residue Chemistry Chapter of the Dicamba RED, DP# 317699, 12/20/05, C. Olinger.

TABLE C.3. Residue Data from Sweet Corn Field Trials with Dicamba.

Trial ID (County, State; Year)	Zone	Crop/ Variety	Commodity	Total Rate (lb ae/A)	PHI	Residues (ppm)[1] [Average]		
						Dicamba	5-OH Dicamba[2]	Combined Residues[3]
Wayne, NY; 2008 (RCN R080608)	1	Sweet Corn/ Serendipity	Forage	0.1268	32	ND ND [<0.01]	ND ND [<0.01]	<0.02 <0.02 [<0.02]
					72	ND ND [<0.01]	ND ND [<0.01]	<0.02 <0.02 [<0.02]
			K+CWHR		32	ND (0.0031) [<0.01]	ND ND [<0.01]	<0.02 <0.02 [<0.02]
					72	ND (0.0027) [<0.01]	ND ND [<0.01]	<0.02 <0.02 [<0.02]
			Immature Stover		72	(0.0049) (0.0032) [<0.01]	0.0351 0.0234 [0.0293]	<0.0451 <0.0334 [<0.0393]
			Stover		88	(0.0035) (0.0035) [<0.01]	0.0131 0.0130 [0.0131]	<0.0231 <0.0230 [<0.0231]
York, NE; 2008 (RCN R080609)	5	Sweet Corn/ Xtra-Tender 272A	Forage	0.1254	32	ND (0.0041) [<0.01]	(0.0061) (0.0081) [<0.01]	<0.02 <0.02 [<0.02]
					63	ND ND [<0.01]	0.0116 (0.0084) [<0.0108]	<0.0216 <0.02 [<0.0208]
			Immature K+CWHR		32	ND ND [<0.01]	ND ND [<0.01]	<0.02 <0.02 [<0.02]
			K+CWHR		63	ND ND [<0.01]	ND ND [<0.01]	<0.02 <0.02 [<0.02]
			Immature Stover		72	ND ND [<0.01]	ND ND [<0.01]	<0.02 <0.02 [<0.02]
			Stover		92	ND ND [<0.01]	(0.0030) ND [<0.01]	<0.02 <0.02 [<0.02]

TABLE C.3. Residue Data from Sweet Corn Field Trials with Dicamba.

Trial ID (County, State; Year)	Zone	Crop/ Variety	Commodity	Total Rate (lb ae/A)	PHI	Residues (ppm)[1] [Average]		
						Dicamba	5-OH Dicamba[2]	Combined Residues[3]
Payette, ID; 2008 (RCN R080610)	11	Sweet Corn/ Bodacious	Forage	0.1264	33	(0.0032) (0.0046) [<0.01]	0.0577 0.0786 [0.0682]	<0.0677 <0.0886 [<0.0782]
					53	(0.0023) ND[4] [<0.01]	0.0588 0.0570[4] [0.0579]	<0.0688 <0.0670 [<0.0679]
			Immature K+CWHR		33	(0.0024)[4] (0.0027) [<0.01]	ND[4] ND [<0.01]	<0.02 <0.02 [<0.02]
			K+CWHR		53	ND ND [<0.01]	ND ND [<0.01]	<0.02 <0.02 [<0.02]
			Immature Stover		72	ND ND [<0.01]	0.0210 0.0176 [0.0193]	<0.0310 <0.0276 [<0.0293]
			Stover		98	ND ND [<0.01]	0.0207 0.0425 [0.0316]	<0.0307 <0.0525 [<0.0416]

[1] ND = Not detected (<LOD). The LOQ = 0.01 ppm and the LOD = 0.002 ppm for all analytes. Values between the LOD and LOQ are reported in parenthesis. Per trial averages are calculated using the LOQ for all residues reported as <LOQ.
[2] Residues of 5-OH dicamba are expressed in parent equivalents as calculated by the registrant using a molecular weight conversion factor of 0.9325.
[3] Combined residues are the sum of dicamba and 5-OH dicamba.
[4] Average of multiple analyses.

TABLE C.4. Summary of Residue Data from Sweet Corn Crop Field Trials with Dicamba.

Commodity	Total App. Rate (lb ae/A)	PHI (days)	Residue Levels (ppm)[1]							
			n	Sample Min.	Sample Max.	LAFT[2]	HAFT[2]	Median	Mean	Std. Dev.
Dicamba										
Forage	0.125-0.127	32-33	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A[3]
		53-72	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Immature K+CWHR		32-33	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
K+CWHR		53-72	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Immature stover		72	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Stover		88-98	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
5-OH Dicamba[4]										
Forage	0.125-0.127	32-33	3	<0.01	0.0786	0.01	0.0682	0.0100	0.0294	0.0336
		53-72	3	<0.01	0.0588	0.01	0.0579	0.0108	0.0262	0.0274
Immature K+CWHR		32-33	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
K+CWHR		53-72	3	<0.01	<0.01	0.01	0.01	0.01	0.01	N/A
Immature stover		72	3	<0.01	0.0351	0.01	0.0293	0.0193	0.0195	0.0097
Stover		88-98	3	<0.01	0.0425	0.01	0.0316	0.0131	0.0182	0.0117

TABLE C.4. Summary of Residue Data from Sweet Corn Crop Field Trials with Dicamba.

Commodity	Total App. Rate (lb ae/A)	PHI (days)	Residue Levels (ppm)[1]							
			n	Sample Min.	Sample Max.	LAFT[2]	HAFT[2]	Median	Mean	Std. Dev.
Combined Residues[5]										
Forage	0.125-0.127	32-33	3	<0.02	0.0886	0.02	0.0782	0.0200	0.0394	0.0336
		53-72	3	<0.02	0.0688	0.02	0.0679	0.0208	0.0362	0.0274
Immature K+CWHR		32-33	3	<0.02	<0.02	0.02	0.02	0.02	0.02	N/A
K+CWHR		53-72	3	<0.02	<0.02	0.02	0.02	0.02	0.02	N/A
Immature stover		72	3	<0.02	0.0451	0.02	0.0393	0.0293	0.0295	0.0097
Stover		88-98	3	<0.02	0.0525	0.02	0.0416	0.0231	0.0282	0.0117

[1] Except for sample min/max, values reflect per trial averages; n = no. of field trials. For calculation of median, mean, and standard deviation, the LOQ (0.01 ppm for all analytes) was used for any results reported as <LOQ in Table C.3.
[2] LAFT = lowest-average-field-trial; HAFT = highest-average-field-trial.
[3] N/A = Not applicable.
[4] Residues of 5-OH dicamba are expressed in parent equivalents as calculated by the registrant using a molecular weight conversion factor of 0.9325.
[5] Combined residues are the sum of dicamba and 5-OH dicamba.

D. CONCLUSION

The submitted sweet corn field trial data are adequate and reflect the use of dicamba (WG formulation) as one foliar broadcast application at a rate of 0.125-0.127 lb ae/A, with PHIs of 32-33 and 53-72 days for forage and K+CWHR and 72 and 88-98 days for stover. Under these conditions, combined residues of dicamba and its metabolite 5-OH dicamba (and per trial maximum) in/on sweet corn forage may be up to 0.0886 ppm (0.0782 ppm) and 0.0688 ppm (0.0679 ppm) at PHIs of 32-33 and 53-72 days, respectively; combined residues of dicamba and 5-OH dicamba (and per trial maximum) in/on stover may be up to 0.0451 ppm (0.0393 ppm) and 0.0525 ppm (0.0416 ppm) at PHIs of 72 and 88-98 days, respectively. Combined residues of dicamba and 5-OH dicamba were below the LOQ (<0.02 ppm) in/on all samples of K+CWHR at PHIs of 32-33 and 53-72 days. An acceptable method was used for dicamba residue quantitation. Adequate data are available to support sample storage intervals and conditions.

There were no unusual weather conditions reported that may have adversely impacted the results of the study. Additionally, it does not appear that the agricultural practices used adversely impacted the results of the study.

E. REFERENCES

DP#: 275611
Subject: PP# 0E6209. Dicamba (Distinct®, EPA Reg #7969-150) on Sweet Corn. Evaluation of Residue Data and Analytical Methods.
From: G. Kramer
To: S. Brothers/R. Forrest
Dated: 7/26/01
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Subject: Dicamba. Residue Chemistry Considerations for the Reregistration Eligibility Decision (RED) Document. Summary of Analytical Chemistry and Residue Data.
From: C. Olinger
To: K. Tyler
Dated: 12/20/05
MRID(s): None

F. DOCUMENT TRACKING

RDI:.
Petition Number(s):
DP Barcode(s): D375578
PC Code: 029801

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